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Nonlinear transport and localization in single-walled carbon nanotubes

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Abstract

We have measured the electrical transport properties of mats of single-walled carbon nanotubes (SWNT) as a function of applied electric and magnetic fields. We find that at low temperatures the resistance as a function of temperature R(T) follows the Mott variable range hopping (VRH) formula for hopping in three dimensions. Measurement of the electric field dependence of the resistance R(E) allows for the determination of the Bohr radius of a localized state a = 700nm. The magnetoresistance (MR) of SWNT mat samples is large and negative at all temperatures and fields studied. The low field negative MR is proportional to H^2, in agreement with variable range hopping in two or three dimensions. 3D VRH indicates good intertube contacts, implying that the localization is due to the disorder experienced by the individual tubes. The 3D localization radius gives a measure of the 1D localization length on the individual tubes, which we estimate to be >700 nm. Implications for the electron-phonon mean free path are discussed.

Keywords: Transport measurements, conductivity, Hall effect, magnetotransport; Fullerenes and derivatives

1. Introduction

Metallic (n,n) single-walled carbon nanotubes (SWNT) are true one-dimensional conductors with unusual electronic properties[1-3]. The existence of only two conduction channels per tube regardless of the radius of the tube is expected to lead to very long 1D localization lengths[4]. Ineffective electron-phonon scattering, similar to in-plane graphite, is predicted to lead to long electron-phonon mean free paths[5,6]. Although transport measurements[7,8] on individual tubes or bundles of tubes show spectacular phenomena such as Coulomb blockade, the insulating contacts and short sample lengths make determination of transport properties difficult. Transport measurements on bulk nanotube samples (mats) should in principle give information about the transport properties of the individual tubes.

Measurements of the resistance R as a function of temperature T on bulk samples (mats) of such tubes indeed show metallic behavior (positive dR/dT) at high temperature, but negative dR/dT at low temperature[9]. The previous lack of understanding of the mechanism leading to the low temperature resistance upturn has prevented the extraction of useful information about the individual nanotubes from the bulk transport data. In this work we present measurement of the resistance as a function of temperature, as well as electric and magnetic fields. The data unambiguously show that the low temperature upturn in resistance is due to localization of charge carriers. The conduction mechanism in the localized regime is three-dimensional variable range hopping (3D VRH), indicating that the inter-tube contacts are good.

The samples used in this study were produced by catalyst-assisted arc-vaporization[10] or laser-vaporization[11] of a graphite source, yielding similar results. The resulting material was purified in HNO_3 to remove catalyst impurities and amorphous carbon, and then washed and filtered. The samples are observed by transmission electron microscopy to consist of bundles of tens or hundreds of tubes arranged in a triangular lattice. The mats consist of a random network of these bundles, connected on a length scale of approximately 100nm. Electrical contact to the mats was made using silver paint in a standard in-line four probe configuration. Typical sample sizes were 3mm x 1mm x 0.05mm. Sample resistances at room temperature ranged from 100 to 3000 Ohms.

2. Temperature-Dependent Resistance

Figure 1 shows the resistance as a function of temperature R(T) for several SWNT samples. The data are plotted on a semi-log scale as a function of $T^{-1/4}$; straight lines on this plot indicate R(T) obeying the form:

$$R(T) = R_0 \exp(T_0/T)^{1/4}. \qquad (1)$$

This form is expected[12] for variable range hopping in three dimensions (3D VRH). Attempts to fit the R(T) data using a different temperature exponent in eq. 1 are markedly poorer. The slopes for the five curves in fig. 1 are all similar, giving a T_0 of approximately 250K. T_0 thus corresponds reasonably with the observed minimum in resistance. One expects eq. 1 to hold only at temperatures below T_0; above T_0 the hopping contribution to the resistance should become temperature independent[12]. This agrees reasonably with what is observed; with scattering included one expects to observe a rise in resistance above T_0.

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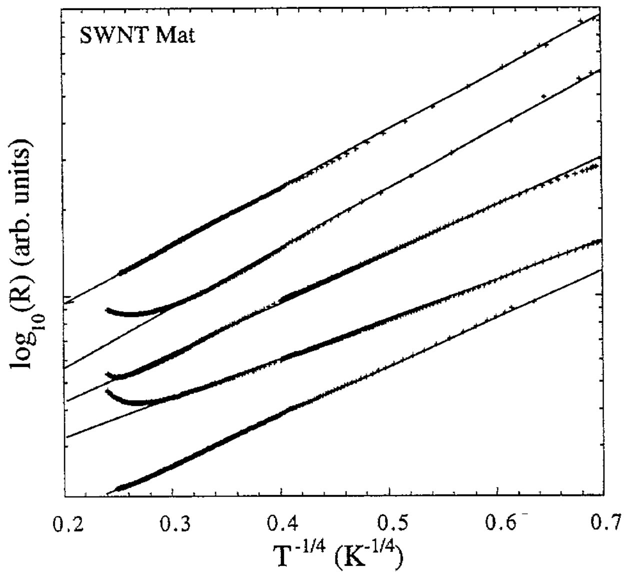

Fig. 1. Resistance of several SWNT mat samples plotted as a function of temperature to the −1/4 power. Curves are offset for clarity. Straight lines are fits to eq. 1.

3. Nonlinear Resistance

The resistance of the SWNT mat was measured at finite electric field using a standard pulsed current technique: 10μsec current pulses were applied to the sample. The current and voltage were monitored simultaneously as a function of time using an oscilloscope, allowing the intrinsic resistance to be separated from (time-dependent) self-heating effects.

Figure 2 shows the R(T) behavior of a SWNT mat at various applied electric fields. The resistance of SWNT mats shows a striking dependence on E; a modest electric field can completely suppress the resistance upturn and recover metallic behavior from 2.2K to 300K.

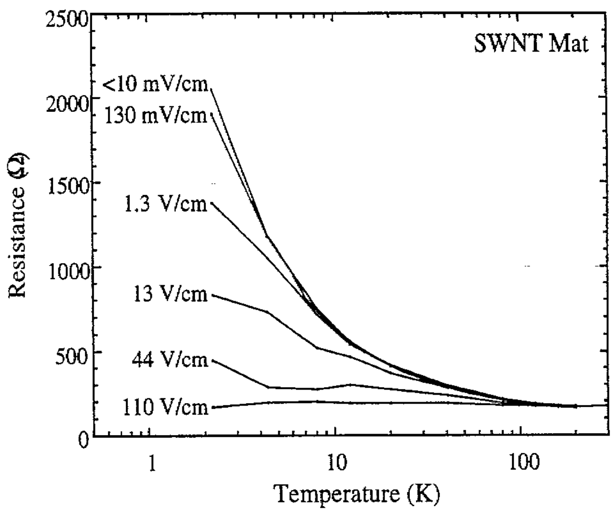

Fig.2. Resistance as a function of temperature for SWNT mat sample at several electric fields.

Nonlinear resistance is expected for localized systems. Temperature and electric field both have a similar delocalizing effect on the carriers. The two energy scales for temperature and electric field are kT and eEa, respectively, where k is Boltzmann's constant, e the electronic charge, and a the Bohr radius of an electronic state. It is found that[13]:

$$R(kT,0) = \frac{R}{2}(0, \frac{3}{8}eEa), \qquad (2)$$

valid for finite values of R. This scaling allows one to determine the localization radius a from a measurement of R(E) at low temperatures and R(T) in the Ohmic regime.

Figure 3 shows R(E) for a SWNT mat sample at temperatures down to 403mK. At low electric fields the R(E) curves are flat, indicating Ohmic behavior. At higher electric fields the resistance is non-linear, and at the highest fields the R(E) curves merge to a temperature-independent behavior. The R(T) data are shown on the same figure, with the temperature scaled by the factor 3.4 in order to match the electric field in V/cm. The scaling of the two curves indicates a = 700nm.

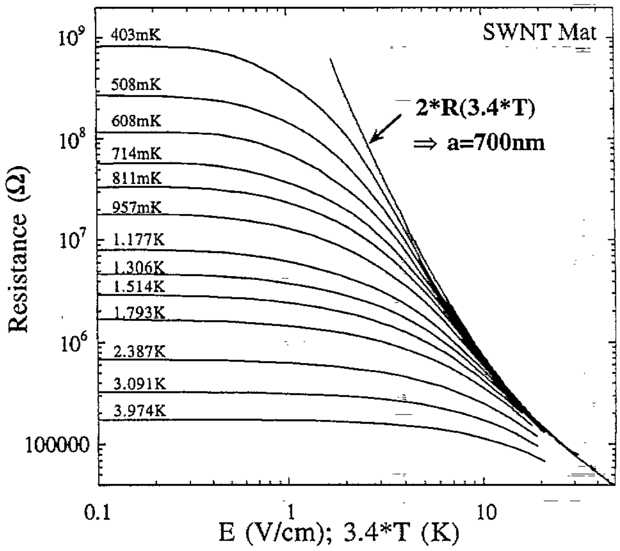

Fig. 3. Resistance as a function of electric field at various temperatures for SWNT mat. Also shown is the resistance as a function of temperature scaled according to eq. 2, giving the radius of localized states a=700nm.

An additional check on the localization radius may be made by examining the low-electric-field R(E). The onset of non-linear resistance should occur at an electric field given by[13]

$$eEa/kT = 0.2. \qquad (3)$$

Figure 4 shows R(E) for the same SWNT mat sample as figure 3. Arrows mark the electric fields at which eq. 3 is satisfied for a=700nm. The onset of non-linearity corresponds well with the prediction of eq.3. The fact that this method, which uses the low-field R(E) agrees with the method of eq. 2, which uses the high-field R(E), is further evidence that self-heating is not a problem in our measurement, and that a=700nm is the correct value.

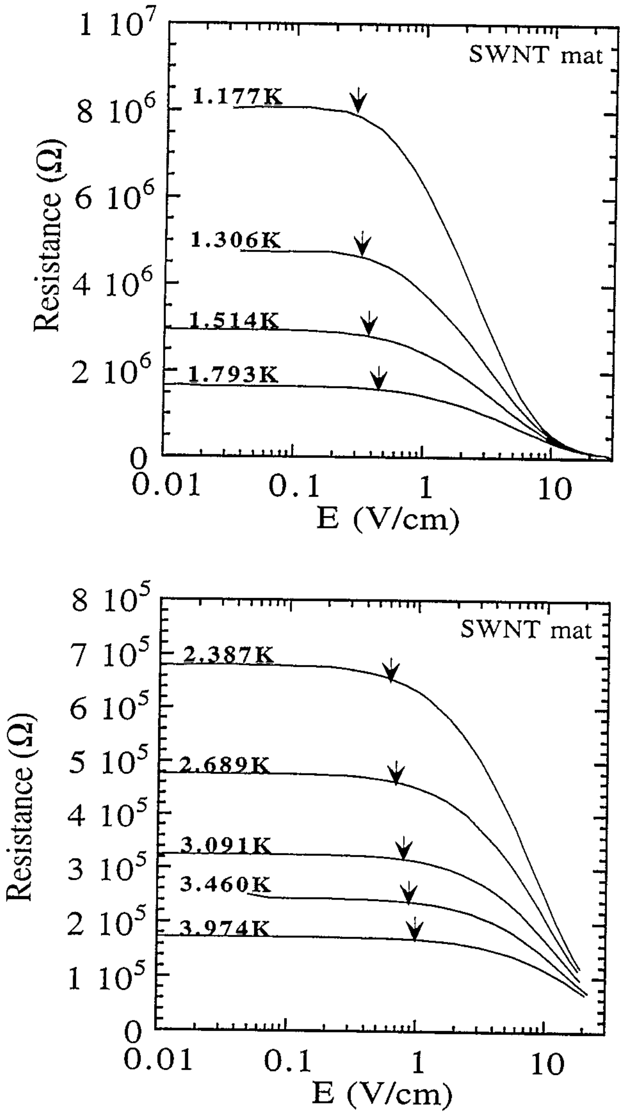

Fig. 4. Resistance as a function of electric field for SWNT mat. Arrows mark the onset of non-linear resistance given by eq. 3.

4. Magnetoresistance

The magnetoresistance of hopping systems stems from two effects. At low fields, the phase between alternate hopping paths enclosing a magnetic flux is changed by the flux, according to the model of Sivan, Entin-Wohlman, and Imry (SEI)[14]. This leads to a negative magnetoresistance, quadratic in magnetic field. At higher magnetic fields, the electronic orbits shrink, leading to positive magnetoresistance[15]. Both effects occur only in two or three dimensions.

Figure 5 shows the magnetoresistance (MR), defined as the change in resistance divided by the resistance at zero field, of a SWNT mat sample at various temperatures. The MR is negative at all fields and temperatures measured, but shows a minimum, increasing at higher fields.

Figure 6 shows the MR data from figure 5, now on a double logarithmic scale. The lines on the plot indicate H^2 dependence of the MR, in agreement with the variable range hopping model of SEI. SEI predict that the magnetic field dependence should saturate when one flux quantum penetrates an area equal to $R^{3/2}\chi^{1/2}$, where R is the average hopping distance and χ the spacing between localized states. Taking $R=700\text{nm}(T_0/T)^{1/4}$ and $\chi=n^{1/3}=0.6\text{nm}$ for metallic (10,10) tubes in a bundle gives the saturation field as 0.6-2.5 Tesla for T=4–120K. This agrees well with the point of deviation from H^2 behavior in figure 6. Similar deviation from H^2 at this saturation field is observed[16] in $CuInSe_2$.

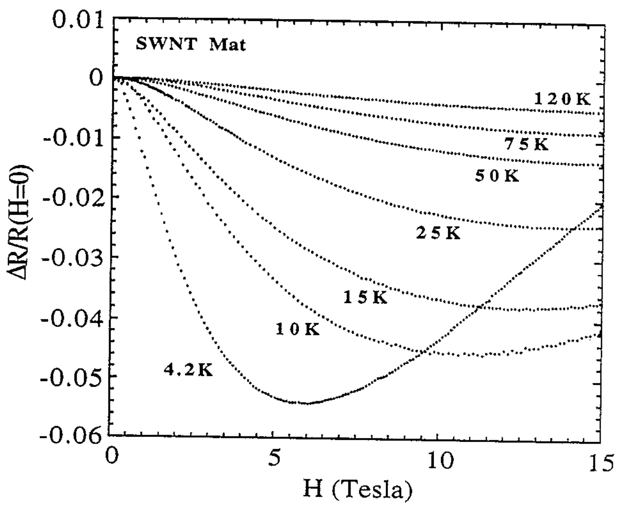

Fig. 5. Magnetoresistance of SWNT mat as a function of magnetic field.

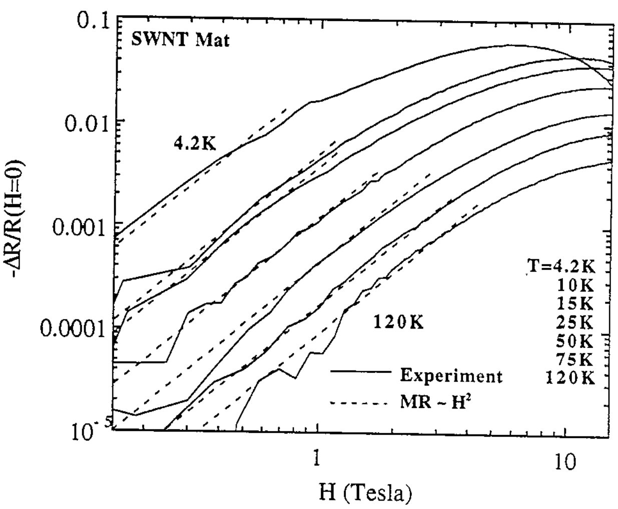

Fig. 6. Magnetoresistance of SWNT mat as a function of magnetic field. Solid lines are data; dotted lines are fits to quadratic magnetic field dependence.

5. Discussion

Both R(T) and R(H) support three-dimensional variable range hopping as the conduction mechanism in SWNT mats.

SWNT mats are localized electronic systems where the electronic states are three-dimensional, with a radius of approximately 700nm, much greater than the average distance between bundle contacts observed by TEM. This result is inconsistent with any model of localization in which the electrons are confined to an individual tube or bundle. The dimensionality in Mott's VRH formula indicates that the number of available states for hopping is proportional to the distance r from the localized state raised to the d power. Hopping confined to a single tube or to nearest-neighbor bundles is one-dimensional, since the number of available states scales linearly with r along the tube. Only if the localized state extended across many tube crossings would the number of available states be proportional to r^3. This implies that the SWNT bundles are well connected, such that individual electronic states in the mat extend across several bundle junctions. We conclude that granularity, i.e. insulating junctions between nanotubes or bundles, cannot be the source of the localization. The spatial decay of the wavefunctions must then occur along the tubes themselves. The 3D radius of the localized states thus gives a measure of the 1D localization length $l_{1D} >$ 700nm. Such long 1D localization lengths are predicted[4] even in the presence of significant disorder, such as would be present in a mat, have been predicted for SWNT.

We may further ask why localization is seen at such a high temperature for such a long localization length? Localization relies on coherence of the electronic wavefunctions over the distance of the localization length. Electron-phonon scattering destroys this coherence, thus the electron-phonon mean free path must be greater than the average hopping distance, at least at temperatures below the resistance minimum, approximately 250K. At 250K $T \approx T_o$, so the average hopping distance is approximately 700nm, so the electron-phonon mean free path is again >700nm. A theoretical calculation[5] for a (5,5) nanotube at 250K gives the mean free path as 1.6μm at 250K; a (10,10) tube should have somewhat more scattering due to the smaller interband spacing, but should still be in agreement with our result.

6. Conclusions

We have measured the electrical transport properties of SWNT mats in electric and magnetic fields. The R(T) and R(H) data indicate that the conduction mechanism in SWNT mats is three dimensional variable range hopping. The temperature and electric field dependence of the resistance allows for a determination of the radius of localized states a≅700nm. We conclude that SWNT are well connected within the mat such that electronic states overlap several tubes. The localization is likely a product of 1D localization on the individual tubes, which allows us to set a lower bound on the 1D localization length of 700nm. The observation of localization up to the relatively high temperature of 250K also gives a similar lower bound for the electron-phonon mean free path at 250K of 700nm. Both of these length scales, though extremely long, are consistent with theoretical estimates for SWNT.

7. Acknowledgements

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8. References

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